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# Electrochemical determination of bentazone using simple screen-printed carbon electrodes



Alemnew Geto<sup>a,1</sup>, Jafar Safaa Noori<sup>a,b,\*</sup>, John Mortensen<sup>c</sup>, Winnie E. Svendsen<sup>b</sup>, Maria Dimaki<sup>b</sup>

<sup>a</sup> IPM – Intelligent Pollutant Monitoring ApS, 2690 Karlslunde, Denmark

<sup>b</sup> Department of Biotechnology and Biomedicine, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

<sup>c</sup> Department of Science and Environment, Roskilde University, 4000 Roskilde, Denmark

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## ABSTRACT

Bentazone is one of the most problematic pesticides polluting groundwater resources. It is on the list of pesticides that are mandatory to analyze at water work controls. The current pesticide measuring approach includes manual water sampling and time-consuming chromatographical quantification of the bentazone content at centralized laboratories. Here, we report the use of an electrochemical approach for analytical determination of bentazone that takes 10 s. The electrochemical electrodes were manually screen printed, resulting in the low-cost fabrication of the sensors. The current response was linearly proportional to the bentazone concentration with a  $R^2 \sim 0.999$ . We demonstrated a sensitivity of  $0.0987 \mu\text{A}/\mu\text{M}$  and a limit of detection of  $0.034 \mu\text{M}$ , which is below the U.S. Health Advisory level. Furthermore, the sensors have proved to be reusable and stable with a drop of only 2% after 15 times reuse. The sensors have been applied to successfully quantify bentazone spiked in real groundwater and lake water. The sensing method presented here is a step towards on-site application of electrochemical detection of pesticides in water sources.

## 1. Introduction

Pesticides are biologically active compounds commonly used in agriculture to increase yield and food production by protecting crops from organisms including insects, plants, fungi, rodents and nematodes (Salman and Al-Saad, 2012). Due to the growing demand for food along with the increasing global population, the use of pesticides has become a common practice (Wang et al., 2015). However, the extensive use of pesticides in global agricultural practices has led to the contamination of water resources, which is a challenge for the preserving and sustaining the environment.

Herbicides are classes of pesticides used to increase agricultural yield and quality by destroying other plants competing with the desired crops. Bentazone (3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one-2,2-dioxide) (BTZN) is one of the widely used post-emergence herbicides to control broad-leaf weeds and sedges in corn fields, rice paddles, and other intensive crops (Bruzzoniti et al., 2016; Mir et al., 2014; Wang et al., 2015). Bentazone has high solubility in water, resistance to hydrolysis and high mobility in soil. It may leach from soil into groundwater, and may contaminate surface water through effluents from production plants, drainage waters and actual water use (Bruzzoniti

et al., 2016). As a result, it is frequently detected in ground and surface waters at concentrations above the European Union (EU) threshold for drinking water ( $0.1 \mu\text{g}/\text{L}$ ) (Cañero et al., 2012; Wang et al., 2015; Noori et al., 2018). The United States Environmental Protection agency has set a health advisory limit of  $0.3 \text{ mg}/\text{L}$  BTZN in drinking water (Environmental Protection Agency, 2012).

Toxicological studies have shown that BTZN is slightly toxic by ingestion and by dermal absorption in mammals (Cho et al., 2017). Reported toxicological symptoms from ingestion of BTZN in humans may include; vomiting, diarrhea, trembling, weakness and irritation to the skin, eyes and the respiratory track (Mir et al., 2014). Large ingested doses of BTZN have also led to acute hepatitis, acute renal failure, and even death (Müller et al., 2003; Škavić et al., 2018). It is thus important to develop a reliable analytical method to determine BTZN at low concentrations in polluted water sources.

Several analytical methods have been reported for the determination of BTZN such as gas chromatography (Mir et al., 2014; Ogierman, 1990), liquid chromatography (Cho et al., 2017; Feng et al., 2016; Fuhrmann et al., 2014; Peschka et al., 2007) and spectrofluorimetric (García Sánchez et al., 1992) techniques. Although these methods are known for their high sensitivity, selectivity and minimum interference,

\* Corresponding author at: IPM – Intelligent Pollutant Monitoring ApS, 2690, Karlslunde, Denmark.

E-mail address: [jasnoo@intpm.dk](mailto:jasnoo@intpm.dk) (J.S. Noori).

<sup>1</sup> Shared first author.

the need for extensive and time-consuming sample preparation steps, such as derivatization, extraction or preconcentration makes them unsuitable for routine environmental monitoring.

Alternatively, electrochemical sensors have been attractive for their simplicity, speed of response, sensitivity, ease of operation and low cost without suffering the limitations of the aforementioned methods (Alatraktchi et al., 2016a, b; Alatraktchi et al., 2014). Hence, some attempts have been made for the electrochemical determination of BTZN using glassy carbon (GCE) (Cerejeira et al., 2002; Manuela Garrido et al., 1998), boron-doped diamond (BDDE) (Jevtić et al., 2018) and electrodes modified using polyaniline/ $\beta$ -cyclodextrine carbon nanotube (PANI- $\beta$ -CD/MWCNT) (Rahemi et al., 2013; Yañez et al., 2010), multi-walled carbon nanotubes-ionic liquid-reduced graphene oxide on a SiC NPs modified carbon ionic liquid electrode (MWCNT-IL/RGO/SiC/CILE) (Norouzi et al., 2015) has been used, as have conducting polymers (Simões et al., 2006) and poly-manganese acetate octakis-(2-diethylaminoethanethiol) phthalocyanine (poly-AcMnODEAETPc) (Akinbulu and Nyokong, 2009). However, the use of bare glassy carbon electrode for the oxidation of BTZN has led to a strong adsorption of oxidation products (Manuela Garrido et al., 1998) limiting its suitability for routine application and causing reproducibility problems.

One solution to such fouling problem is the use of disposable screen-printed electrodes (SPEs). SPEs consist of a chemically inert substrate on which the working, pseudo-reference and counter electrodes are printed through screen printing technology. The screen-printing technology has numerous advantages, including design flexibility, the ability to process automation and excellent reproducibility. Moreover, a wide range of printing inks can be employed, resulting in extremely versatile devices that can be applied to the selective determination of several compounds (Couto et al., 2016). As a result, screen-printed electrochemical sensors are already in wide use for applications in clinical, environmental and food analysis (Trojanowicz, 2016).

The aim of this work is therefore, to develop a sensitive, simple and robust in-house produced electrochemical sensor based on screen-printing technology for the determination of BTZN in real water samples. To the best of our knowledge, there is no previous report on the electrochemical determination of BNTZ using screen-printing method.

## 2. Materials and methods

### 2.1. Reagents

All chemicals used in the study were analytical grade and were used without any prior treatment. Characterization was conducted in 10 mM ferri/ferro cyanide in phosphate buffer saline (PBS) by mixing Potassium hexacyanoferrate(II) trihydrate (P23289-110G, Sigma-Aldrich, Denmark) and Potassium hexacyanoferrate(III) (31253-250G, Sigma-Aldrich, Denmark). Bentazone was supplied by Sigma-Aldrich and a stock solution of 10 mM was prepared in 96% Ethanol (VWR, 18F274005, France). The BTZN stock solution was kept in a brown bottle wrapped in aluminum foil to avoid light exposure. All electrochemical studies were conducted by diluting appropriate volumes of the stock solution in buffer solutions. All aqueous solutions were prepared in ultra-pure Milli-Q water of resistivity of 18.2  $\Omega$  m. Mesotrione, Chlorobenzene, 4-chlorobenzaldehyde, 1,3,5-Trichlorobenzene were purchased from Sigma Aldrich Chemie, 33,855-100MG-R, 284513-100ML, 112,216-50G, T54607-100G respectively. All potentially interfering compounds were prepared by making a stock solution of 10 mM and diluting it further to the required concentration. Carbon ink (No. CH-8, Jujo chemicals CO., Ltd., Japan) was used to produce the sensor electrodes. The sensor substrate used in this study was Kapton tape (Kapton 500HN, Lohmann, UK).

### 2.2. Instruments and measurements

The pH measurements were conducted using a pH meter (EUTECH

Instruments pH 700, Singapore). The conductivity of the aqueous solutions was measured using a multimeter (Meter Lab CDM210, Radiometer Copenhagen, Lyon, France). All electrochemical measurements were performed by PalmSens4 Potentiostat, equipped with PSTrace 5.5 software (PalmSens BV, Netherlands). Square Wave Voltammetry (SWV) was conducted at  $E_{step} = 5$  mV; Amplitude = 50 mV; and frequency 10.0 Hz. The quantification measurement was tested on concentrations from 50 to 0.19  $\mu$ M of BTZN. Three replicates were conducted for each concentration. The limit of detection (LoD) and quantification (LoQ) were calculated from the calibration curve using the equation:  $LoD = 3 \times SD/m$  and  $LoQ = 10 \times SD/m$  where  $m$  is the slope of the calibration curve and  $SD$  is the associated standard deviation.

Measurements in the presence of different interfering compounds were conducted by fixing the BTZN concentration to 5  $\mu$ M and introducing three different concentrations of the interfering compounds: 1, 5 and 10  $\mu$ M. The interfering compounds were selected on the basis of either having a similar molecular structure to BNTZ or on the likelihood of these chemicals to be present in the water sample.

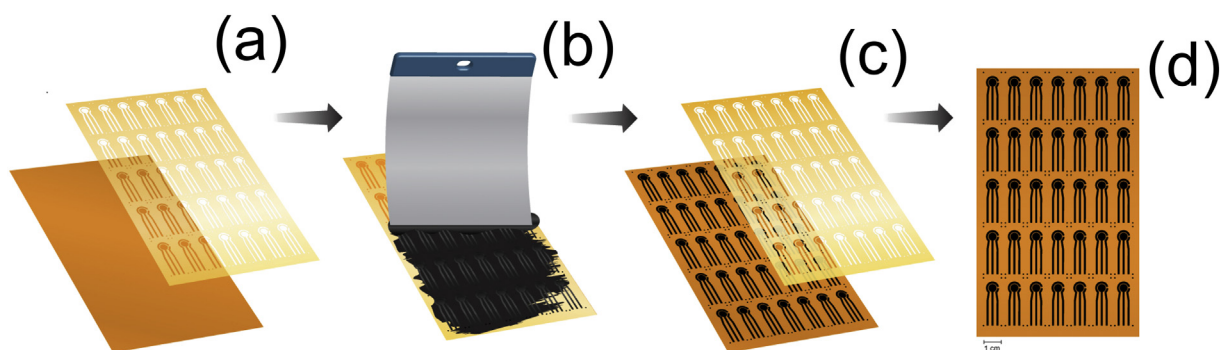
Unprocessed water from two different locations was also tested in this study. The first sample was taken from groundwater from a local water producer (Gevninge Vandværk, Denmark). The water sample was collected immediately after pumping from the well and used with no further treatment. The sample was always stored in a dark fridge at 4 °C in a closed container.

The second sample was collected from a local lake in Kgs. Lyngby, Denmark. The lake water was filtered using a simple coffee filter prior to use and the sample was stored at 4 °C. Then, 2 mL of each sample were added to 8 mL of the buffer solution and the pH of the mixture was adjusted to 7. Then, the mixtures were spiked with standard BTZN to reach the required three concentrations of 1, 5 and 10  $\mu$ M. The lake water was filtered using simple coffee filter prior to use and the sample was stored at 4 °C. Both samples were added to the buffer and spiked with BTZN to reach the required three different concentrations of 1, 5 and 10  $\mu$ M. The spiked water samples were allowed to reach room temperature prior to testing. For each measurement, the electrodes were covered with 70  $\mu$ L of the sample. Each set of data was collected on one fresh sensor, starting the measurement from low to high concentrations.

To analyze the reproducibility of the measurements, 22 sensors from different fabrication batches were tested on 5  $\mu$ M BTZN concentration. To evaluate the sensor performance, first we conducted repetitive measurements using one sensor at a BTZN concentration of 6  $\mu$ M to observe the signal stability. In this test the sensor was simply wiped with a cleaning tissue and new fresh sample was applied on the electrode surface. The second repeatability test was conducted using a 3  $\mu$ M BTZN concentration using another fresh sensor. In this test, the electrodes were flushed with Milli-Q water and dried with nitrogen prior to each new measurement. The morphology of the sensors was studied using FEI Quanta 200 ESEM FEG, UK.

### 2.3. Fabrication of the sensor

The following described fabrication process is a slight modification from a previously reported process (Alatraktchi et al., 2018). A three-electrode configuration design consisting of a working electrode (WE), a counter electrode (CE) and a reference electrode (RE) was applied in this study. The electrodes were designed in SolidWorks 2017 with comparable dimensions to commercially available sensors provided by DropSens DRP 110. The pattern was cut in 0.05 mm thick plastic foil using a CO<sub>2</sub> laser cutter (Epilog Laser mini, 30w, USA), thereby forming a shadow mask. The shadow mask was placed on top of the Kapton substrate and ink was placed on top of it. The electrodes would form after manually scraping the ink on top of the shadow mask, followed by removing the shadow mask. The ink was let to cure on a hot plate overnight at 25 °C. The low curing temperature prevents the ink solvent



**Fig. 1.** Sensor fabrication process. (a) placement of the mask on the substrate, (b) manual swiping of the ink on top of the substrate/mask sandwich, (c) removal of the mask layer, (d) sensor electrodes printed on Kapton substrate ready for use.

from deforming the Kapton substrate. The fabrication process is illustrated in Fig. 1. The sensors were characterized by measuring 10 mM ferri/ferrocyanide using cyclic voltammetry (CV) from  $-1.0$  to  $1.0$  V at different scan rates between 10 and 100 mV/s.

### 3. Results and discussion

#### 3.1. Electrochemical characterization of sensor

The performance of the fabricated sensor was evaluated by conducting CVs on ferri/ferrocyanide at different scan rates (Fig. 2a). The peak currents were extracted from the CVs and plotted as function of the square root of the scan rate (Fig. 2b). The fitted line has an  $R^2$  value of 0.9745, which fulfills one of the requirements for a reliable electrochemical sensor (Bard and Faulkner, 2001). The numeric ratio between the anodic and cathodic peak currents is approximately 1, hereby fulfilling another requirement for a reliable system. The measured potential separation is around 59 mV for all tested scan rates, however; the position of the peak potential is dependent on the scan rate, which makes the electrochemical sensor only quasi-reversible. This means that the sensor is ineligible for studying electrochemical kinetic reactions, but can be used for reliable analytical measurements. The fabricated electrode was electrochemically compared with the commercial DRP-110 in 10 mM ferri/ferrocyanide solution. The midpoint ( $E_{1/2}$ ) potential of the ferri/ferro redox couple was calculated as  $E_{1/2} = (E_{pa} + E_{pc})/2$ . The results show a 20 mV negative shift of the midpotential for the fabricated screen printed electrode relative to the commercial DRP-110 electrode. Despite the fact that the two electrodes employ different pseudo-reference electrodes the difference in the midpotential of the ferri/ferrocyanide redox couple is not significantly different. The surface morphology of the fabricated and commercial electrodes were also investigated using scanning electron microscopy as shown in (Fig 3a and b), respectively. In both cases, the electrode surfaces are very rough, with scattered small cavities of various dimensions covered with nets of graphitic carbon. This offers a high surface area for the redox

reaction in addition to enhanced adsorption capacity for pre-concentration resulting in a better performance of the electrode.

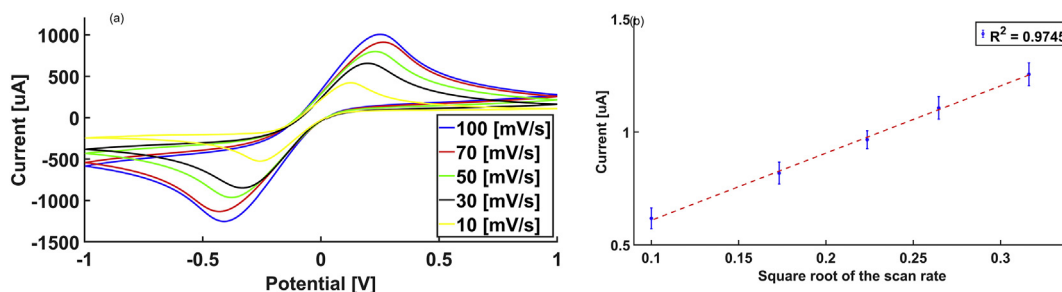
#### 3.2. Electrochemical behavior of bentazone at the screen-printed carbon electrode

The electrochemical response of BTZN was measured against the background solution to investigate if the observed signal was due to the BTZN. It can clearly be seen from Fig. 4 that there is no response from the background and a very clear signal appearing for the BTZN at a potential around 0.7 V.

#### 3.3. Effect of pH

The influence of pH on the oxidation of BTZN at the SPE was examined by SWV in phosphate buffer solutions (PBS) with pH ranging from 5 to 9. Background and 5  $\mu$ M BTZN sample measurements for each buffer was performed at a fresh SPE. As can be seen from the background corrected voltammograms (Fig. 5a) and corresponding peak current and potential plot against pH (Fig. 5b), the oxidation of BTZN at the SPE is dependent on the pH of the medium. An increase in pH from 5 to 8 led to a gain in peak current and a decrease afterwards. A significant increase in the measured current at pH 8 is also observed. Preliminary tests in buffers less than pH 5 yield poorly defined and weak voltammetric peaks. Since BTZN is a weak acid ( $pK_a \sim 3.3$ ), 99 mol percentage of it exists in anionic form in pH 6–7 (Ania and Béguin, 2007).

The peak potential also showed a positive shift at a rate of 59.9 mV/pH ( $R^2 = 0.969$ ) between pH 5 and 8 which indicates proton participation in the oxidation of BTZN. This observation supports proton coupled electron transfer oxidation process of BTZN. Contrary to this, previous reports showed absence of peak potential dependence on pH at BDDE (Jevtić et al., 2018) and PANI- $\beta$ -CD/MWCNT/GCE (Rahemi et al., 2013). A negative shift of peak potential at a rate of 40 mV/pH was reported at GCE below pH 4 which became independent at higher pH



**Fig. 2.** Electrochemical characterization of the screen-printed electrodes. (a) cyclic voltammogram obtained from testing 10 mM ferri/ferro cyanide at 5 different scan rates. (b) Peak current vs. square root of the scan rates denoting a quasi-reversible system suitable for electrochemical quantification. All measurements have been repeated 3 times on new sensors. All measurements have been conducted versus the carbon electrode as a pseudo-reference electrode.



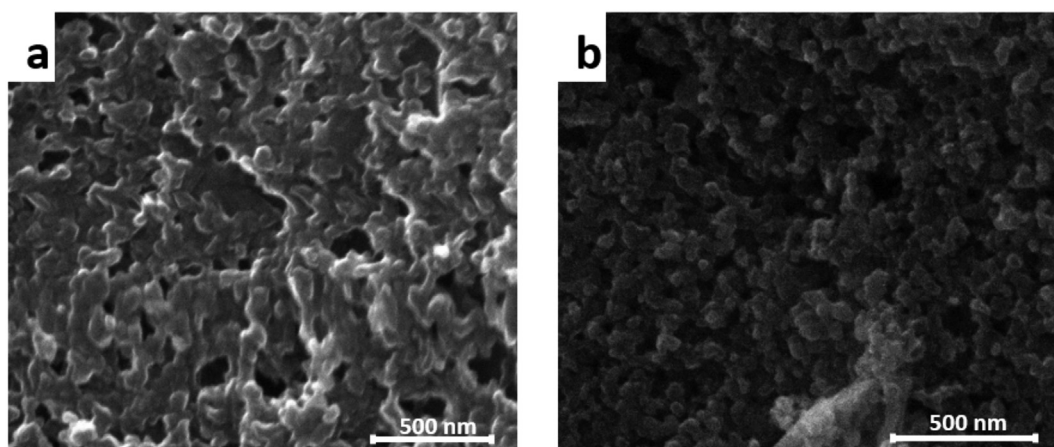


Fig. 3. Scanning electron microscopic (SEM) images of fabricated (a) and commercial DRP -110 (b) screen-printed carbon electrodes.

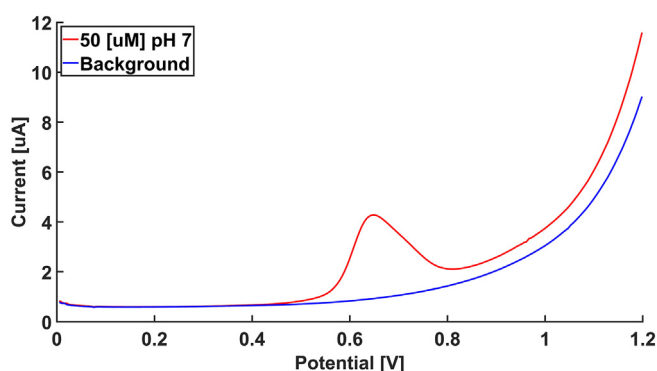


Fig. 4. Square wave voltammetry for 50  $\mu\text{M}$  bentazone in 0.1 M phosphate buffer solution pH 7 vs. the background.

range (Manuela Garrido et al., 1998). Moreover, earlier studies have reported higher peak currents for BTZN detection using GCE and BDDE at pH 4 and PANI- $\beta$ -CD/MWCNT/GCE at pH 6 due to weaker interaction of deprotonated BTZN with the electrode surface.

The mechanism of BTZN oxidation is thought to proceed at the nitrogen end of the tertiary amine due to the higher electron density of the lone pairs of the nitrogen (Rahemi et al., 2013). The difference observed in the peak potential and current dependence obtained at the SPE and other electrodes could be attributed to the effect of pH in altering the electrode surface of the electrode materials through functional group dissociation. Even though the maximum current was obtained at pH 8 using SPE, it was decided to conduct all further measurements on a neutral pH 7 since it mimics natural conditions.

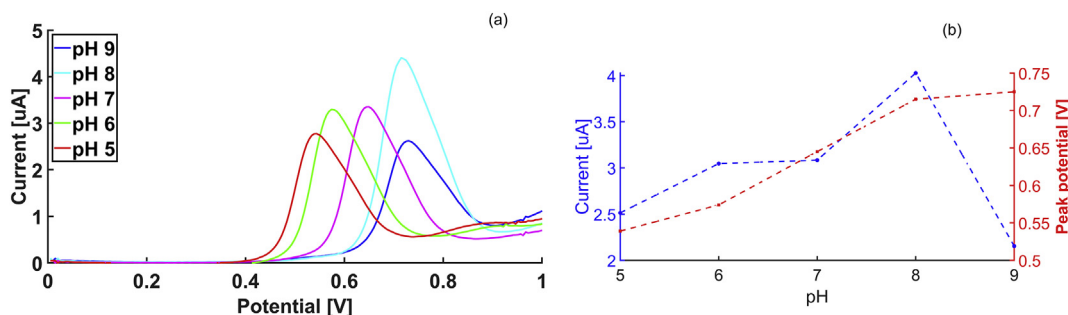


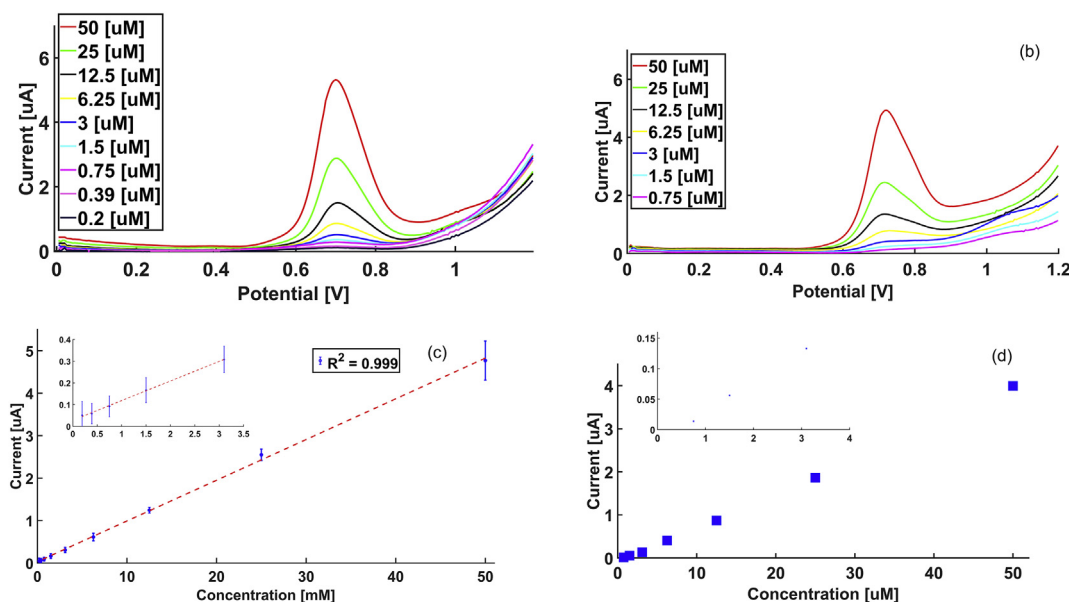
Fig. 5. Square wave voltammograms (a) and corresponding plots of peak current and peak potential against pH (b) obtained for 50  $\mu\text{M}$  BTZN in buffer solutions of pH 5–9.

### 3.4. Calibration curve

The performance of the SPE in measuring different concentrations of BTZN was investigated using SWV in PBS of pH 7. A linear increase in the oxidation current with increasing BTZN concentrations was observed in the voltammograms and the respective calibration plot, as depicted in Fig. 6a. The linear regression equation,  $I_p(\mu\text{A}) = 0.0987 c(\mu\text{M}) + 0.0176$  ( $R^2 = 0.999$ ) was established from three sets of independent measurements over the BTZN concentration range of 0.19  $\mu\text{M}$  to 50  $\mu\text{M}$ . The limit of detection (LoD) = 0.034  $\mu\text{M}$  and quantification (LoQ) = 0.112  $\mu\text{M}$  were calculated from the calibration curve. The LoD of the SPE is significantly lower than reports of BTZN detection with BDDE (Jevtić et al., 2018), GCE (Cerejeira et al., 2002; Manuela Garrido et al., 1998), Poly-AcMnODEAETPC/GCE (Akinbulu and Nyokong, 2009), PANI- $\beta$ -CD/MWCNT/GCE (Rahemi et al., 2013) and comparable to MWCNT-IL/RGO/SiC/CILE (Norouzi et al., 2015). The upper linear range of the calibration curve is limited by peak distortion and poor signal reproducibility, which could probably be due to adsorption of oxidation products on the electrode surface upon repetitive measurements. A summary of analytical parameters and comparison with other electrochemical methods for the determination of BTZN at SPE is shown in Tables 1 and 2, respectively. Commercially available carbon sensor electrodes from DropSens (DRP-110) were tested on the same set of samples and under the same conditions, Fig. 6b. The commercially available sensors can only measure down to 0.75  $\mu\text{M}$  compared to 0.19  $\mu\text{M}$  measured by the SPE however; the oxidation peak for BTZN at both electrodes appears at around the same potential, which is in agreement with the ferri/ferrocyanide study under section 3.1.

### 3.5. Evaluation of sensor performance

To evaluate the sensor performance from different produced



**Fig. 6.** Measurement of bentazone (BTZN) using square wave voltammetry (SWV). (a) SWVs for BTZN detection using SPE in 0.1 M PBS, pH 7. (b) SWVs for BTZN detection using commercially available screen-printed carbon electrodes (DRP-110) in 0.1 M PBS, pH 7. (c) Plot of peak currents vs. concentrations of BTZN using SPE. The inset presents a zoom in of the concentrations between 0.19 to 3.1  $\mu\text{M}$ . (d) Plot of peak current vs. concentration of BTZN using DRP-110. The inset presents a zoom in of the concentrations between 0.39 to 3.1  $\mu\text{M}$ .

batches, 28 sensors from 4 different batches fabricated over 4 months were tested by measuring a constant BTZN concentration, Fig. 7. The current response was not normally distributed, possibly due to the sensor fabrication procedure in addition to the small number of statistical data points required for a normal distribution. The shadow mask was not reusable; thus, a new mask was used after producing each sheet. This alone introduced a variation in the total surface area of the electrodes which could result in differences in the measured current. Even within the same batch, different forces applied during the printing process would result in different edge rounding and eventually different electrode surface areas. To have a uniformly distributed current and higher reproducibility of the signal than obtained in Fig. 7, we could implement automatic control of the screen-printing process for producing the sensors, e.g. using a mesh screen as a shadow mask and using a screen-printing machine to distribute the ink uniformly over the mesh.

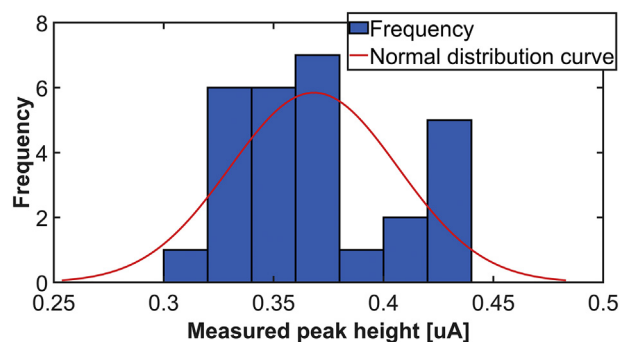
Another test was conducted to evaluate the continuous operation of the same sensor. Two tests were performed, one testing the sensor by repetitive measurements without washing, and the other including a washing step after each measurement of the same BTZN concentration. The repeatability of both tests demonstrates a stable sensor and all the measurements were within 10% range of the relative standard deviation (%RSD). For the test with no washing step applied, the RSD was 5.4% while for the test with washing step the RSD was 7.52%. The tests indicate the possibility of reusing the sensor in real applications.

**Table 1**  
Comparison of performance parameters for electrochemical detection of bentazone.

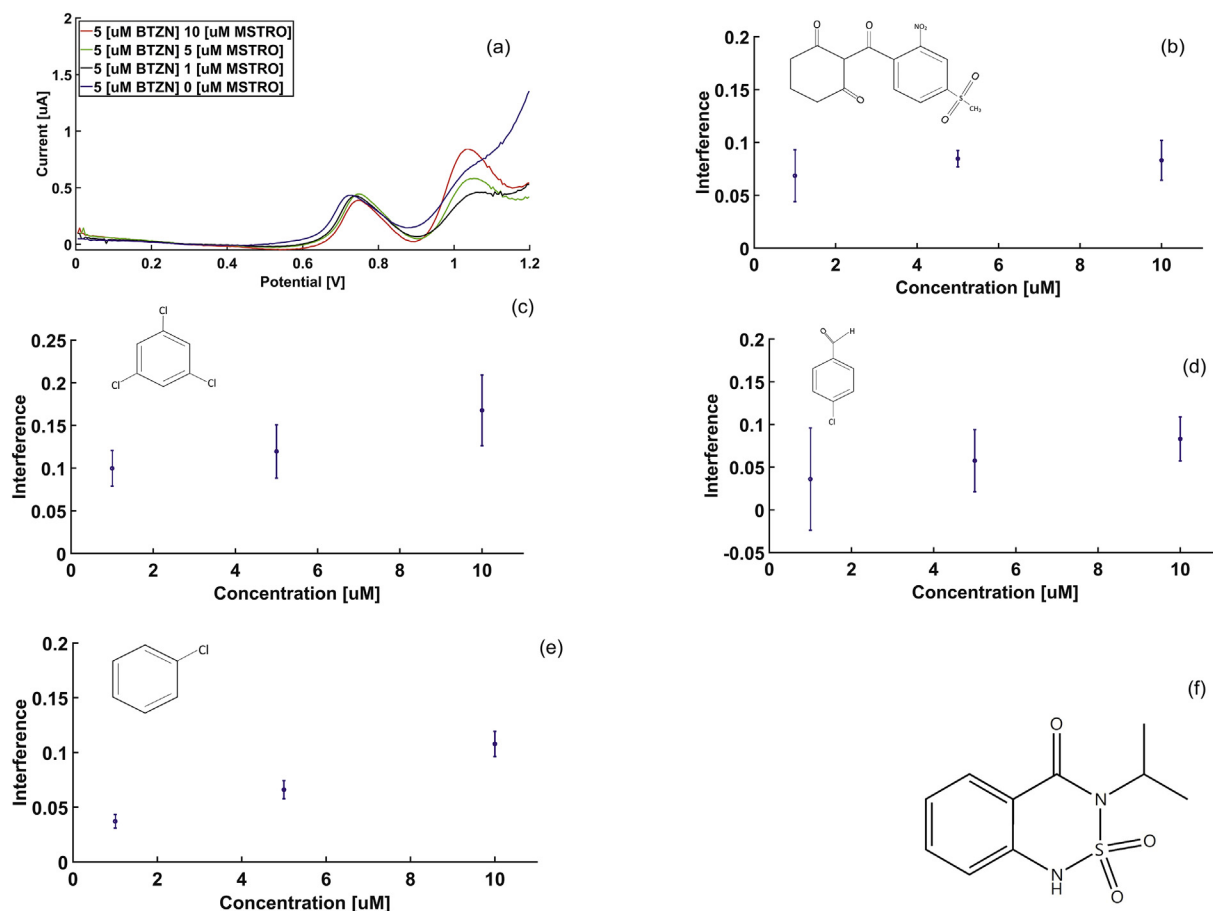
Electrode	Method	Linear range	Detection limit	Ref.
GCE	SWV	15.1–22.6 $\mu\text{M}$	10 $\mu\text{M}$	Manuela Garrido et al. (1998)
MWCNT-IL/RGO/SiC/CILE	CV	1–150 nM	0.25 nM	Norouzi et al. (2015)
PANI- $\beta$ -CD/MWCNT/GCE	CV	10–80 $\mu\text{M}$	1.6 $\mu\text{M}$	Rahemi et al. (2013)
BDDE	DPV	2–100 $\mu\text{M}$	0.5 $\mu\text{M}$	Jevtić et al. (2018)
Poly-AcMnODEAETPC/GCE	SWV	50–750 $\mu\text{M}$	0.25 $\mu\text{M}$	Akinbulu and Nyokong (2009)
GCE	FIA/Amperometry	2.5–50 $\mu\text{M}$	1 $\mu\text{M}$	Cerejeira et al. (2002)
DRP-110	SWV	0.75–50 $\mu\text{M}$	0.042 $\mu\text{M}$	This study
SPE	SWV	0.19–50 $\mu\text{M}$	0.034 $\mu\text{M}$	This study

**Table 2**  
Analytical parameters of BTZN determination at SPE using SWV in PBS, pH 7.0.

Parameter	Value
Peak potential	0.715 V
Linear range	0.19–50 $\mu\text{M}$
Repeatability (%RSD) (C = 6 $\mu\text{M}$ , n = 23)	5.4%
Reproducibility (%RSD) (C = 5 $\mu\text{M}$ , n = 28)	10.4%
Limit of detection (LoD)	0.034 $\mu\text{M}$
Limit of quantification (LoQ)	0.112 $\mu\text{M}$



**Fig. 7.** Evaluation of the fabricated sensor produced from 4 different batches at different dates. Variation of the measured current from 28 sensors.



**Fig. 8.** Interference tests on four different compounds at three different concentrations of 1, 5 and 10  $\mu\text{M}$  in the presence of a constant bentazone concentration of 5  $\mu\text{M}$ . (a) signal obtained when measuring bentazone in the presence and absence of mesotrione. Interference rate on the bentazone signal in the presence of (b) mesotrione, (c) 1,3,5-Trichlorobenzene, (d) 4-chlorobenzaldehyde and (e) chlorobenzene, (f) Bentazone molecular structure.

### 3.6. Selectivity test

To investigate the selectivity of the method proposed in this study, the interference from four relevant compounds was measured. Mesotrione was chosen as it has a chemical structure similar to BTZN, while 1,3,5-Trichlorobenzene, 4-Chlorobenzaldehyde and Chlorobenzene might occur in water resources. The interference was determined by adding the interfering chemical to a BTZN solution and measuring with the same SWV used to quantify BTZN. It can be seen from Fig. 8a that Mesotrione has a separate distinguishable peak that comes in a separate potential around 1 V. Although the concentration of Mesotrione is increased, the effect on the peak current of BTZN remains unchanged as apparent in Fig. 8b. This suggests that despite appearance of chemical structures very close to the structure of BTZN, the proposed method will still be selective towards the target pesticide. Similarly, 1,3,5-Trichlorobenzene and 4-Chlorobenzaldehyde showed statistically no increased current as function of increased concentration, Fig. 8c,d. However, chlorobenzene showed interference of  $\sim 10\%$  when increasing the concentration to 10  $\mu\text{M}$ , Fig. 8e. All samples had a pH of  $7 \pm 0.05$ . pH tests confirmed there was no pH change after adding the interferants.

The matrix effect on the compound detection refers to the effect of the solution components on the measured signal. When changing the composition of the solution in which BTZN is detected, the measured BTZN signal may be suppressed (Lezi and Economou, 2015). However, despite the addition of interfering pesticides to concentrations higher than the BTZN concentration, it was still possible to determine BTZN with none to minor signal suppression. Thus, the interference measurements show that new calibration graphs accounting for severe

matrix effects can be conducted to accurately quantify BTZN despite the presence of other pesticides in the samples.

### 3.7. Real sample analysis

The method was applied on real water samples by spiking three different BTZN concentrations in water from groundwater with a conductivity of 144.7  $\mu\text{S}/\text{cm}$  (Fig. 9a) and in lake water with a conductivity of 173  $\mu\text{S}/\text{cm}$  (Fig. 9b). The measured peak current was linearly proportional with the BTZN concentration when testing both water types. Although the curves have a slope difference from the calibration curve in Fig. 4, the two curves in Fig. 9 have the exact same slope. The difference between the lake and groundwater versus the calibration curve obtained in milli-Q water is probably due to the difference in the mineral composition, which have resulted in different conductivities and differences in carrying the current. In further studies, it will be interesting to investigate whether the same calibration curve can be applied for all real water like groundwater and lake water from different sources or if it is necessary to create a correction factor for the specific water sources.

## 4. Conclusion

In this work, it was possible to establish a method for direct detection of bentazone using in-house fabricated screen printed sensors. The repeatability of the measurements was demonstrated to be achieved with high reliability. The selectivity and the repeatability allow future deployment of the sensor in the field for on-site bentazone quantification. The U.S. Health advisory has set a limit of 0.3 mg/L

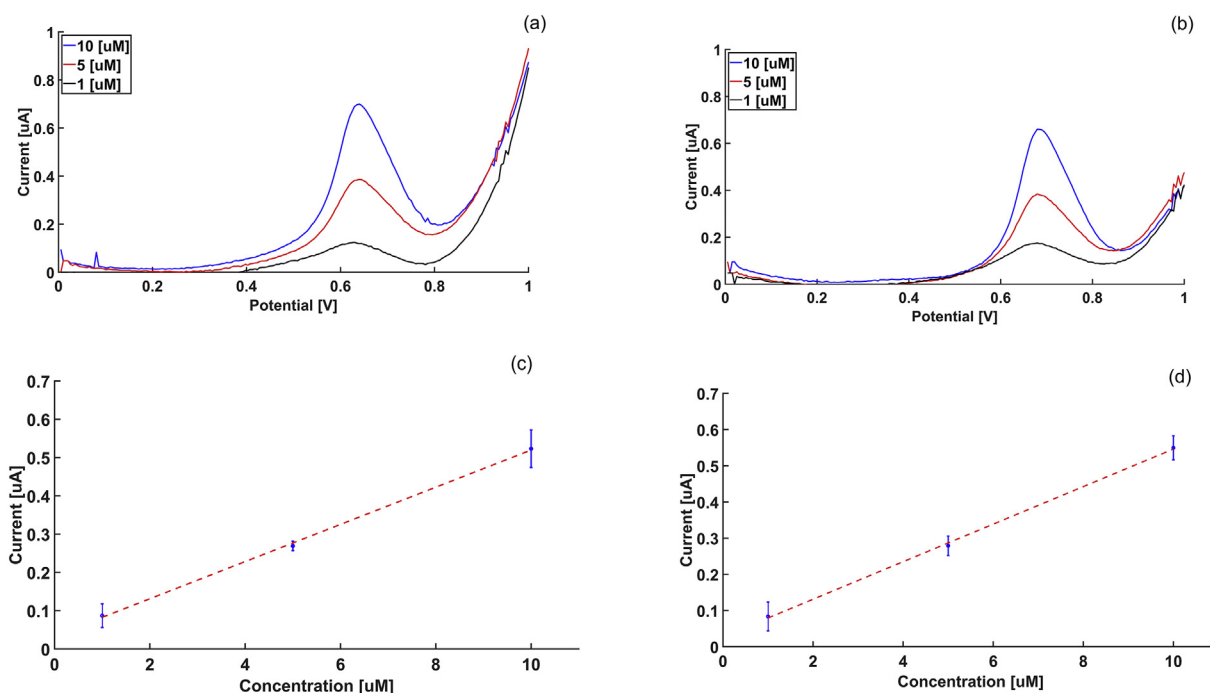


Fig. 9. Square wave voltammograms of three different bentazone concentrations spiked in (a) groundwater and (b) lake water samples. Extracted peak currents for (c) groundwater and (d) lake water, showing linear dependency on the bentazone concentration.

BTZN in drinking water, which is a value this detection approach is already capable of meeting. Further improvements to the sensor fabrication will enable reaching the EU regulation limit of 0.1 µg/L. The work demonstrated in this study is an important step towards a simple and low-cost approach for on-site detection of BTZN in water resources. The work demonstrated in this study represents an early step towards a simple and low-cost approach for on-site detection of BTZN in water resources. Further work needs to be conducted to enhance the detection limit which could be done by surface modification of the electrode.

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